Pore-Network Model Applied to Wormhole Formation in Limestone Resulting from Injection of Carbon Dioxide

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ABSTRACT

Pore-scale spatial heterogeneities can have a significant effect on flow and reaction, in some cases resulting in the formation of "wormholes" through reactive instabilities. In this work a 3-D pore-network model is used to investigate phenomena occurring at the pore scale during geologic sequestration of carbon dioxide. Recently we have modified the reactive flow and transport code FLOTRAN to accommodate a pore network model for fully saturated conditions. FLOTRAN is based on continuum scale mass and energy conservation equations in porous media, and takes into account reactive transport equations that describe multi-component chemical reactions. Such reactions can result in dissolution or precipitation of minerals thereby affecting the porosity and permeability of the formation. In this work we study the formation of "wormholes" in three spatial dimensions during carbon dioxide injection in limestone rocks. The obtained dissolution patterns are compared qualitatively against core-scale experiments performed recently at the NM Institute of Technology (PRRC, Grigg and Svec, unpub.), where carbon dioxide was injected into limestone cores (diameter=5 cm and length=20 cm approximately). Core imaging performed at UC Davis (Lesher and Wilding, unpub.), enable three-dimensional mapping of the "wormholes" formed during the flooding experiments.

1. Introduction

In order to better understand and quantify many flow and transport processes in porous media (e.g. soil remediation strategies, reactive transport, CO_2 sequestration, etc.) it is important to acquire a detailed knowledge of phenomena occurring at the pore-level scale, since they play a key role in the dynamics of multiphase flow and transport/reaction in porous media. Pore networks can provide such a fundamental understanding of detailed processes and/or mechanisms of phenomena occurring at the pore scale and they can assist in identifying key parameters for the system. Pore networks can also be utilized to study the effects of pore-scale structures and processes on macroscopic coefficients (e.g. diffusivity, permeability, reactivity, etc.). They have been used extensively to simulate single or multiphase flow in porous media and phase change phenomena [e.g. Liquid-to-Gas (evaporation/drying), Gas-to-Liquid (condensation, adsorption), Solid-to-Liquid/Gas (hydrate dissociation, solid melting), etc.). Of interest also is their application to study chemical reactions (dissolution/precipitation) in porous media. Reactions can result in altering the available space to flow inside the porous medium. Dissolution can result in increasing the pore space and on certain occasions can produce "wormholes" that provide dominant pathways to the flow. Precipitation, on the other hand, can reduce significantly the permeability of the medium.

2. Motivation

The motivation for this work is briefly presented in this section.
- CO_2 has been identified as a major contributor to the global warming problem.
- Studies have been undertaken to investigate possible solutions involving removing/disposal of the produced CO_2.
- Geologic sequestration (see Fig. 1 for a schematic) is viewed as a very promising disposal method. During this approach CO_2 is going to be injected into oil reservoirs/saline aquifers.
- Other proposed methods include: oceanic disposal at different ocean depths, and injection into off-shore/on-shore hydrate containing sediments with simultaneous CH_4.

Figure 1 also depicts the different length scales that someone can choose to study. While field-scale simulations are essential for final decision-making, we should not forget that input (after appropriate upscaling) from smaller scales (e.g. pore level, molecular level, etc.), can contribute significantly, since their results can improve the continuum field-scale models.

The main objective of the current study is to develop a 3-D Pore-Network Module for the flow and reactive transport continuum model *FLOTRAN*, which utilizes:
- Well-tested numerical solvers
- Unstructured and structured grid capabilities
- Extensive thermodynamic database
- Coupled flow and reaction mode

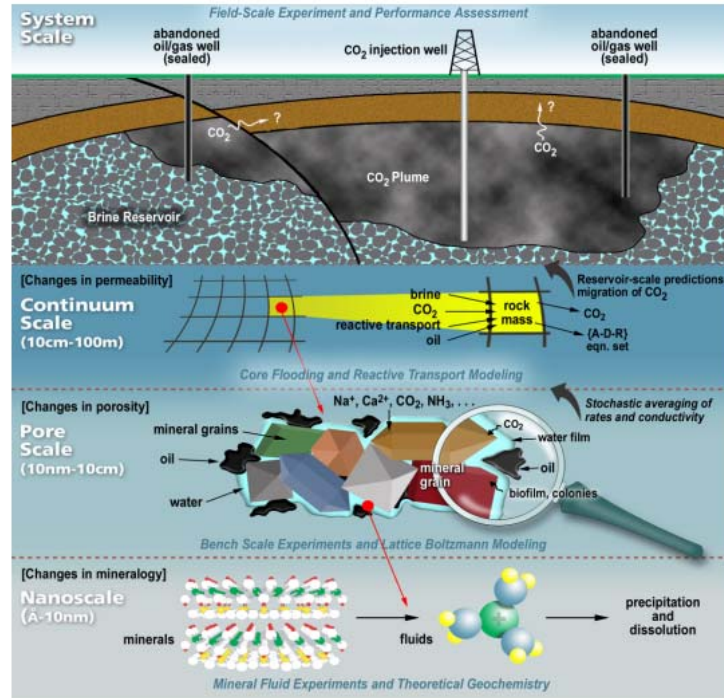This effort is described in the sections that follow.

Figure 1. Schematic of the interplay of the different length scales during geologic sequestration.

3. Approach

We consider the injection of a saturated aqueous solution of CO_2 into a 3-D pore network that represents the initial part, where the injection takes place, of a limestone core used at the N.M. Tech. Experiments (Grigg and Svec, unpub.), with approximate dimensions: diameter=5 cm and length=20 cm.

The regular pore network considered is made-up of 32x32x64 EBB's (Elemental Building Block). Tsimpanogiannis et al. (2005) have discussed the concept of the Elemental Building Block (EBB) which is a regular solid block that has embedded at the center a pore and a number of throats emanating from it (see Fig. 2 for a schematic). A porous medium consists of an ensemble of EBB's. Pores and throats can be of various geometries and their sizes can follow some given distribution.

The pore network was chosen such that the surface area of the injection face is equal to the surface area of the cylindrical cores that were used at the N.M. Tech. experiments. The network consists of spherical pores and cylindrical throats with a diameter ratio equal to 10. Values were randomly distributed using a uniform distribution with a maximum pore diameter equal to 1.38 mm. The considered system has, thus, overall dimensions equal to 4.4 cm X 4.4 cm X 8.8 cm.

Figure 3 shows the correspondence between the pore-network model and the continuum model equations. Figure 4 depicts the chemical-reactions network considered in this study for the limestone dissolution. Also shown are the primary and secondary species that participate in the reactions.

In the results shown here, we consider fluid saturated with CO_2 that is injected along the K-axis with a flow rate of ~180 m/y and pH=4. The results that follow correspond to three time intervals after 10, 20, and 40 days of CO_2 injection.
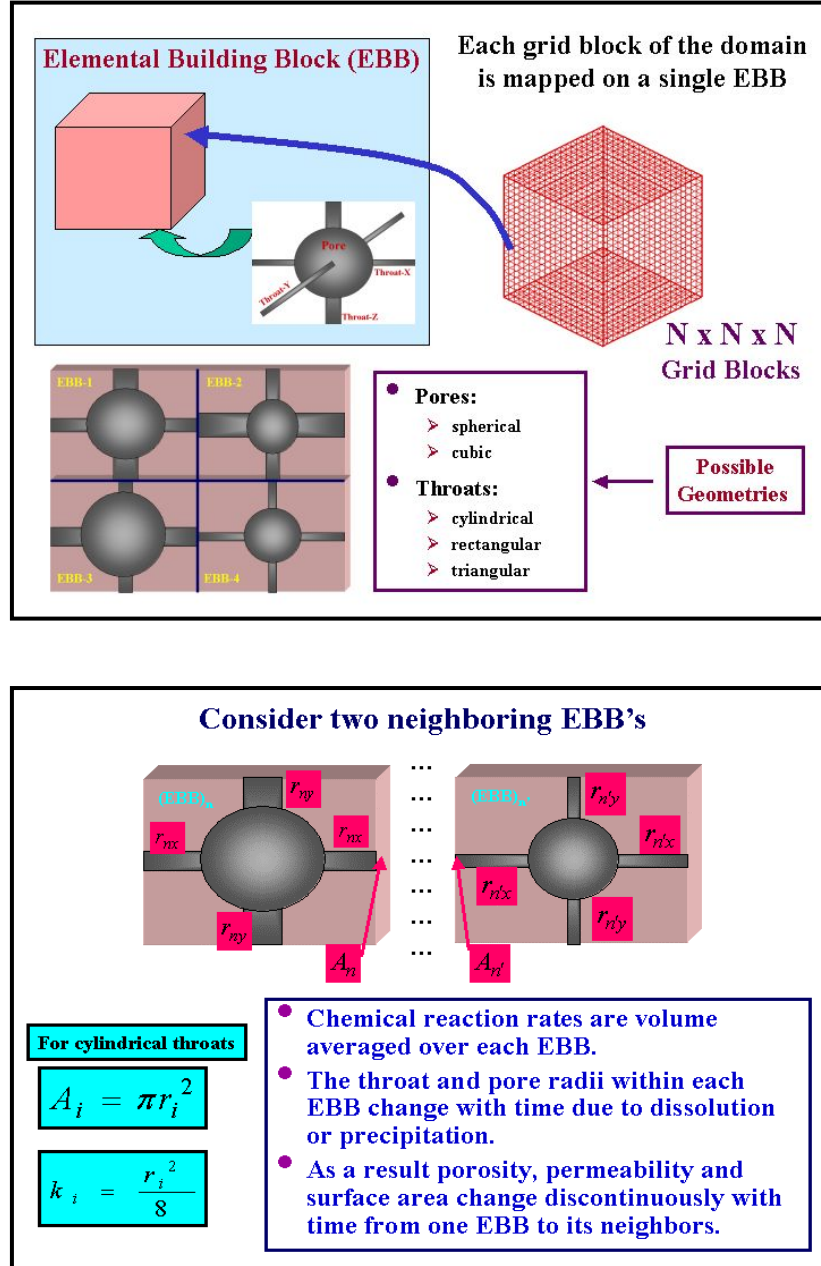
4. Conceptual Model

Figure 2. Schematic of the conceptual model used in this study.

5. Mathematical Formulation

Pore Network Model

$$\sum_{n'} Q_{nn'} = 0$$

$$Q_{nn'} = G_{nn'}^{PN}\Delta P_{nn'} = A_n q_n = A_{n'} q_{n'}$$

$$G_{nn'}^{PN} = \left(\frac{\rho}{\mu l}\right)\left(\frac{2 A_n A_{n'} k_n k_{n'}}{A_n k_n + A_{n'} k_{n'}}\right)$$

$$V_n^P \frac{\Delta \phi_n C_n}{\Delta t} + \sum_{n'}\left((qC)_{nn'} + J_{nn'}^{PN}\right)A_{nn'}^{PN} = V_n \Re^{PN}$$

Continuum Model

$$\frac{\partial}{\partial t}\phi\rho + \nabla \cdot \rho q = 0$$

$$\frac{\Delta \phi\rho}{\Delta t} + \sum_{n'}(\rho q)_{nn'} A_{nn'}^C = 0$$

$$Q_{nn'} = G_{nn'}^C \Delta P_{nn'} = (\rho q)_{nn'} A_{nn'}^C$$

$$G_{nn'}^C = \left(\frac{\rho}{\mu l}\right)A_{nn'}^C\left(\frac{2 k_n k_{n'}}{k_n + k_{n'}}\right)$$

$$\frac{\partial \phi C}{\partial t} + \nabla \cdot (qC - \phi\tau D\nabla C) = \Re$$

$$V_n \frac{\Delta \phi_n C_n}{\Delta t} + \sum_{n'}\left((qC)_{nn'} + J_{nn'}^C\right)A_{nn'}^C = V_n \Re^C$$

Figure 3. Pore-network model equations and the corresponding continuum model equations.

6. Chemical Description

- Injection of CO_2 saturated fluid into a limestone host rock.
- Initially, the system is at equilibrium with atmospheric CO_2 and calcite with pH=8.27.
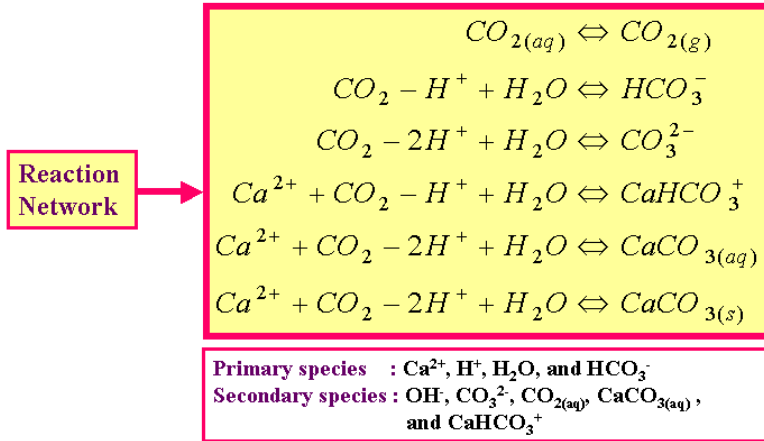- Fluid saturated with CO_2 is injected at 100 bars with pH=4.0.

Reaction Network

$$CO_{2(aq)} \Leftrightarrow CO_{2(g)}$$

$$CO_2 - H^+ + H_2O \Leftrightarrow HCO_3^-$$

$$CO_2 - 2H^+ + H_2O \Leftrightarrow CO_3^{2-}$$

$$Ca^{2+} + CO_2 - H^+ + H_2O \Leftrightarrow CaHCO_3^+$$

$$Ca^{2+} + CO_2 - 2H^+ + H_2O \Leftrightarrow CaCO_{3(aq)}$$

$$Ca^{2+} + CO_2 - 2H^+ + H_2O \Leftrightarrow CaCO_{3(s)}$$

Primary species : Ca^{2+}, H^+, H_2O, and HCO_3^-
Secondary species : OH^-, CO_3^{2-}, $CO_{2(aq)}$, $CaCO_{3(aq)}$, and $CaHCO_3^+$

Figure 4. The system of chemical reactions used in this study.

7. Results

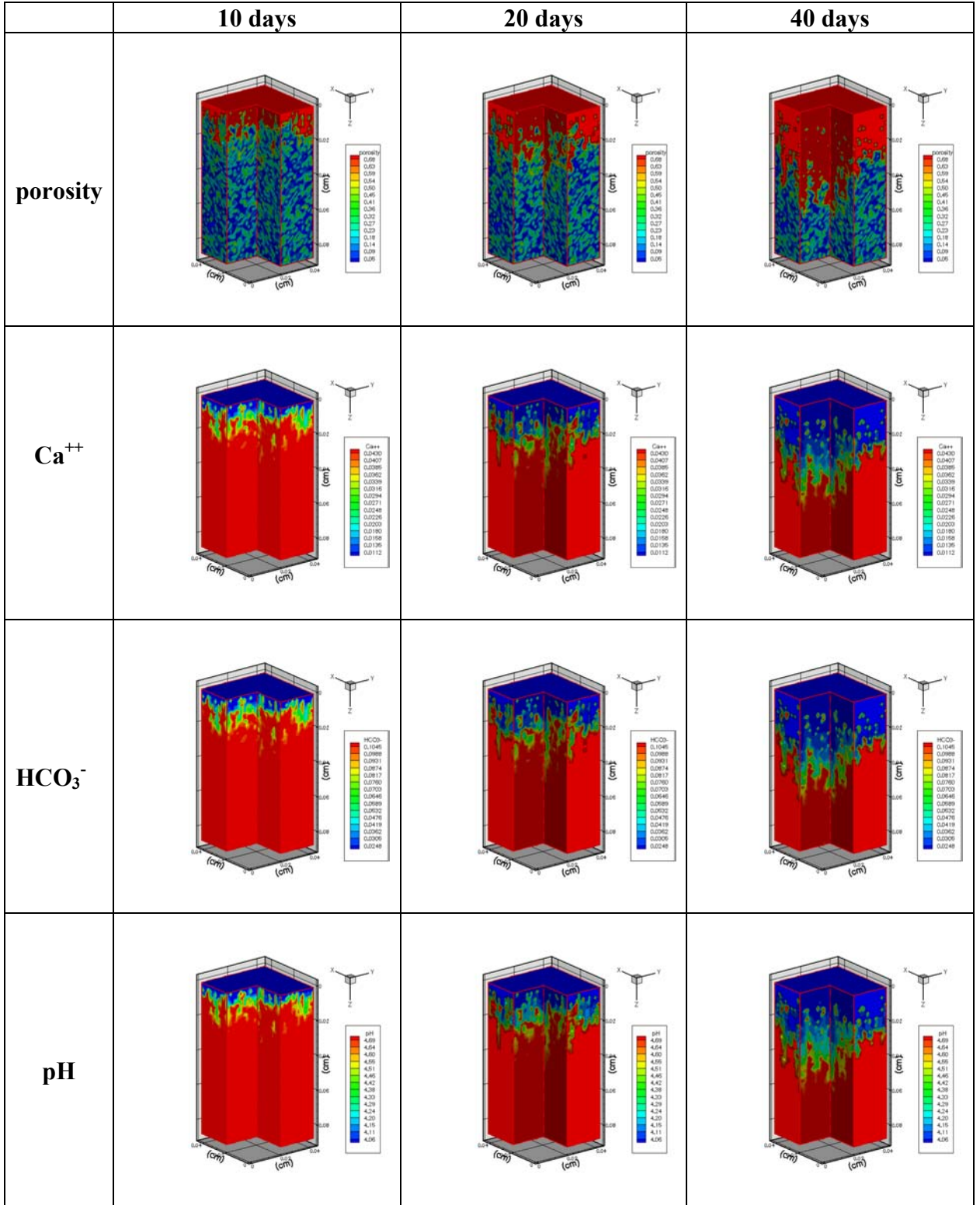|	10 days	20 days	40 days
porosity			
Ca^{++}			
HCO$_3^-$			
pH			

Figure 5. Evolution of porosity, Ca^{++}**,** HCO$_3^-$, pH, at three different time intervals.

8. Discussion

Figure 5 shows the results (invasion patterns) obtained for the evolution of porosity, Ca^{++}, HCO_3^-, pH, at three different time intervals. A brief discussion of the obtained results is presented in this section.

- For the parameters considered in this study we observe the formation of several short (of almost equal length) "wormholes", without, however, the formation of a dominant "wormhole", as occurs during the experiments.
- Complete dissolution of the medium is observed at the face where the injection takes place.
- Further refinement of the model parameters is required to reproduce the experiments more accurately.
- The effect of two-phase flow in the system needs to be carefully examined.
- pH values change about 0.7 units within the range of 3-5 cm.
- Reactions occur at a front that has a characteristic width.

9. Conclusions

The conclusions of this study can be summarized as follows:

- We extended the recently developed Pore-Network module for *FLOTRAN* (Tsimpanogiannis et al., 2005) to 3-D and demonstrated the feasibility of the proposed conceptual model by providing a comparison with core-flooding experiments.
- We applied the 3-D model to the problem of CO_2 injection into a limestone host rock.
- We observed the development of *"wormholing"* features (not possible for "traditional" continuum models). The developed *"wormholes"* have ramified characteristics.
- The presence of local chemical "micro-environments", at the pore-network scale, suggest that upscaling (using the traditional volume-averaging techniques) can be questionable.
- It is expected that a hybrid model may be required to capture the detailed physics at different scales.

10. Future Outlook

The present study is an advancement and a contribution towards the general effort of better understanding the reaction, inside porous media, problem. However, additional work is required. In this section we present some future directions that seem worth

examining. Some of the suggested directions are currently under investigation by our research group.

- ❑ Extend the 3-D simulations to parallel implementation using *PFLOTRAN*. This extension will also enable the consideration of multiple phases in the system (currently only one phase available).
- ❑ Examine more complex geometries including the case of unstructured grids.
- ❑ Consider two-phase system with injection of supercritical CO_2.
- ❑ Examine more complex chemical systems with precipitation and dissolution.
- ❑ Parametric study of the reaction front and "wormhole" formation as a function of Peclet and Damkholer numbers.
- ❑ Study the scaling of the reaction-front width as a function of the problem parameters.
- ❑ Other…

Acknowledgements

References

Tsimpanogiannis, I. N., P. C. Lichtner, and C. Lu (2005), Pore-Network Approach for Upscaling Continuum Reactive Transport Equations, EoS Trans. AGU, 86(52), Fall Meet. Suppl., Abstract H42A-06.